

PERFORMANCE OF HYBRID CATALYST SYSTEM IN TWO-STAGE COAL LIQUEFACTION

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INTRODUCTION

The Clean Coal Research Center at Wilsonville has developed alternate technologies for producing low cost fuels from coal. Process developments of close-coupled integrated (CC-ITSL) configurations using the thermal/catalytic or catalytic/catalytic mode of operation were discussed in earlier articles^{1,2}.

This paper is primarily focused on the low-rank Black Thunder subbituminous coal performance at steady-state operation with catalyst replacement in the thermal/catalytic mode. Process development results from four runs are discussed: Runs 258, 260, 262 and 263. Three different operation modes with supported, dispersed slurry and hybrid catalyst systems were tested. Runs 258 and 260 studied the supported catalyst system using Shell (or Criterion) 324 catalyst in the second stage without addition of a dispersed catalyst. Runs 262 and 263 (second part) tested the hybrid system using a dispersed molybdenum (Molyvan L or 822 precursor) and Criterion 324 supported catalyst in the second stage. Run 263 (first part) tested the dispersed slurry catalyst system using Molyvan L and 822 as precursors. Half-volume reactors were used for Runs 258, 262 and 263; a combination of full- and 3/4-volume reactors was used for Run 260. Iron-oxide (+ dimethyl disulfide) addition was 1-2 wt % MF coal.

The primary objective of this study was to maximize the distillate production with good quality in order to improve the process economics. High distillate yield and coal throughput increase the distillate production. The distillate production can be enhanced by improving coal reactivity, catalyst conversion activity, and distillate selectivity. The performance of a dispersed molybdenum catalyst was evaluated processing a low-rank coal. Solids buildup in reactor transfer lines and interstage separator was investigated for possible reduction or elimination by using a dispersed molybdenum catalyst. The dispersed molybdenum catalyst may give acceptable conversions at moderate reaction temperatures and reduce the coking reactions, that cause solids to deposit in the transfer lines, by hydrogenating thermally produced free radicals and possibly through the prevention of retrogressive reactions³. Dispersed molybdenum catalysts using Molyvan L and Mo octoate as precursors were tested in bench-scale two-stage liquefaction with Illinois No. 6 coal using Amocat 1C bimodal supported catalyst by Amoco Oil Company⁴, and UOP⁵ and Dow Chemical Company⁶ studied dispersed catalysts in bench-scale single stage. Several investigators have studied with dispersed molybdenum and iron catalysts to improve liquefaction conversion and their results can be found in the literature⁷⁻¹⁵. Typical analyses of Black Thunder coal processed for this study are summarized in Table 1. Properties of Shell (or Criterion) Ni-Mo catalyst and dispersed molybdenum precursors tested are shown in Table 2.

PROCESS DESCRIPTION

The current catalytic close-coupled integrated two-stage liquefaction (CC-ITSL) process consists of two H-OIL[®] ebullated-bed reactors and a Residuum Oil Supercritical Extraction-Solids Rejection (ROSE-SRSM) unit¹⁴. Both the reactor designs utilize "H-OIL[®]" technology supplied by Hydrocarbon Research, Inc. The ebullated-bed design helps to maintain a uniform temperature distribution in the reactor. The reactor is used as a thermal reactor in the thermal mode of operation without a supported catalyst. The ROSE-SRSM is a proprietary extraction process at conditions close to the critical point of the deashing solvent. It was developed and licensed by the Kerr-McGee Corporation.

RUN EXPERIMENTS

Key process variables studied in Runs 258, 260, 262 and 263 are listed below to maximize the distillate production by increasing distillate yield and coal throughput processing Black Thunder subbituminous coal.

- (1) Catalyst activity
 - Shell (or Criterion) 324 unimodal supported
 - dispersed molybdenum (Molyvan L/822 precursors)
 - iron-oxide + DMDS (dimethyl disulfide)
- (2) Steady-state operation with catalyst replacement
 - 1.5 to 3 lb/ton MF coal in catalytic stage
- (3) Molybdenum addition concentration (100-1000ppm MF coal)
- (4) Iron-oxide addition concentration (1-2 wt % MF coal)
- (5) Recycle resid concentration
 - 35-45 wt % in the process solvent
- (6) High/low thermal severity mode
- (7) Heavy vacuum gas oil recycle
- (8) Coal space velocity
 - 45-110 lb MF coal/hr/ft³-catalyst in catalytic
 - 30-90 (x1/C) lb MF coal/hr/ft³-reactor in thermal
 - (C: constant equating thermal to catalytic reaction volume in the thermal/catalytic mode)
- (9) Reaction temperature
 - 760-860/760-810°F in the first/second stage
- (10) Inlet hydrogen partial pressure
 - 2450-2850 psia in the first stage
 - 2400-2550 psia in the second stage
- (11) Slurry composition (25-30 wt % coal, 20 wt % CI)
- (12) Interstage separation
- (13) Reactor operation parameters
 - temperature profiles, exotherms
 - ebullation rate, gas flow, slurry flow
 - slurry viscosity, etc.

Several steady-state operation periods in Runs 258, 262 and 263 with half-volume reactors in operation were selected for comparison of distillate production in three different operation modes with the supported, dispersed slurry and hybrid catalyst systems. Experimental results with Black Thunder subbituminous coal are summarized in the following along with the theoretical distillate production projected for the "all-distillate" product slate with resid extinction using a CSTR first order kinetic model¹⁵. Illinois No. 6 bituminous coal result from Run 257J using Amocat 1C in the catalytic/catalytic mode is also included for comparison.

run	catalyst	temper. (°F)	cat. rep. (lb/t MF)	recycle resid (wt %)	dist.prod. (lb/hr)	
		1st/2nd	1st/2nd		exp.	the. ^a
(1)	w/ supported catalyst in the second stage					
258H	Shell 324	840/790	-/1.5	40	127	126
258I	Shell 324	850/790	-/1.5	40	132	126
(2)	w/ dispersed molybdenum slurry catalyst					
262F ^b	Molyvan L	825/810	200 ^c	40	152	137
263E	Molyvan L	840/810	100 ^c	40	147	150
263H	Molyvan 822	840/810	100 ^c	45	150	158
(3)	w/ hybrid catalyst with dispersed and supported catalysts					
262E	^d	825/810	-/3 ^e	40	185	181
263I	^d	840/810	-/3 ^e	45	195	207
263J	^d	840/810	-/3 ^e	40	188	197
(4)	w/ Illinois coal in catalytic/catalytic mode					
257J	Amocat 1C	810/760	3/1.5	50	137	133

^a Using CSTR 1st order kinetic model for resid extinction¹⁵.

^b Some Criterion catalyst was left in the second reactor.

^c Unit: ppm based on MF coal.

^d With a combination of Molyvan L and Criterion 324.

^e Molyvan L addition at 100 ppm based on MF coal.

RESULTS AND DISCUSSION

DISTILLATE PRODUCTION COMPARISON

Supported, Dispersed Slurry and Hybrid Catalyst Systems

The hybrid system (Runs 262E and 263IJ) with a combination of dispersed molybdenum and Criterion supported catalysts showed the highest distillate production, 185-195 lb/hr, among three catalyst systems tested. Corresponding coal space velocities for these runs were 59-62 MF lb/hr-ft³-catalyst in 2nd stage or 24-26 (x1/C) MF lb/hr-ft³-reactors in CCR unit. The distillate production of the hybrid system was 30% higher than that of the dispersed molybdenum slurry catalyst system (147-152 lb/hr in Runs 262F and 263EH at 20 (x1/C) coal space velocity); 50-60% higher than that of the Criterion supported catalyst system (127-132 lb/hr in Run 258H1 at 17 (x1/C) coal space velocity).

The hybrid system with Black Thunder subbituminous coal in the thermal/catalytic mode of operation produced 40-55% higher distillate than the Amocat 1C supported catalyst system with Illinois No. 6 bituminous coal in the catalytic/catalytic mode of operation (Run 257J at 18 (x1/C) coal space velocity). This result suggests that Black Thunder subbituminous coal can produce more distillate than Illinois No. 6 bituminous coal, if process operating conditions are optimized for better coal and resid conversions, even though subbituminous coal has lower distillate yield and selectivity. It seems that due to the addition of the dispersed molybdenum to the supported catalyst system, the hybrid system enhances the distillate production by improving coal and resid conversions, employing higher thermal severity compared to Run 257J with Illinois coal and Amocat 1C catalyst. However, as reported in the previous Run 261 with Illinois bituminous coal using a new bimodal supported catalyst (EXP-AO-60)¹⁵ in the catalytic/catalytic mode with full-volume reactors in operation, the

low/high severity operation significantly improved the distillate production by approximately 40-50%, employing higher thermal severity, increased recycle resid concentration and higher catalyst replacement. Further studies are required for better comparison with bituminous coals using half-volume reactors in operation.

Distillate Product Yield and Selectivity

The addition of a dispersed molybdenum allowed operation at lower thermal severity in the first stage, while the second stage operated at higher thermal severity compared to the supported catalyst system, resulting in higher C4+ distillate product yield and selectivity to resid + UC conversion as summarized below. The potential C4+ distillate yield is estimated by adjusting the resid yield for the "all-distillate" product slate with resid extinction by using an achievable common organic rejection (OR) and distillate selectivity measured in each run.

run	catalyst system	distillate yield, experimental	wt % MAF coal theoretical (OR)	distillate selectivity, %
258HI	supported	55-58	60 (14)	64-68
263EH	slurry	61	62-63 (14)	72-73
263IJ	hybrid	58-61	61-62 (13-14)	71-72

EFFECT OF MOLYBDENUM CONCENTRATION

Varying the molybdenum concentration from 100 to 1000 ppm (based on MF coal) seemed not to affect the resid + UC conversion, but increasing the molybdenum concentration slightly improved coal conversion. Good performance was observed at a low 100 ppm concentration in both slurry and hybrid catalyst systems. Distillate properties were generally the same within the range of molybdenum concentration studied.

The addition of Molyvan L or 822 as a dispersed molybdenum seemed to improve the overall two-stage resid and coal conversions allowing lower temperature and higher space velocity operation. In the hybrid system, with a combination of dispersed and supported catalysts, the resid + UC conversion was 5-10 wt % MAF coal higher and the coal conversion was 3-5 wt % higher than using the catalysts separately, when compared at the same thermal reaction severity operation. The use of just dispersed slurry catalyst (Molyvan L or 822) or Criterion supported catalyst gave similar overall two-stage coal and resid + UC conversions, and conversions improved by the combination of Criterion and Molyvan L or 822 catalysts.

COAL CONVERSION AND ORGANIC REJECTION

Figure 1 illustrates the effect of coal conversion on organic rejection. A good linear correlation was observed with low-rank coals and are summarized as follows.

$$Y = 173.3 - 1.69 X; r^2 = 0.84$$

where Y is the organic rejection (wt % MAF coal), X is the coal conversion (wt % MAF coal), and r^2 is the determination coefficient. The X-intercept in Figure 1 indicates that a deeply cleaned coal could achieve a low organic rejection (4 wt % MAF coal), if extrapolated to 100 wt % coal conversion. A similar observation with bituminous coals was reported in the previous work^{2,15}.

CATALYST AND THERMAL ACTIVITIES IN RESID + UC CONVERSION

Supported catalyst and thermal activities were calculated assuming that the resid + UC conversion reaction follows first-order kinetics for a continuous stirred tank reactor². Cracking activity (resid conversion) is not the only function of the catalyst. Hydrogenation activity of the catalyst was not considered in these catalyst activity analyses. Catalyst activity analysis is based on the overall activity of combined catalytic and thermal conversions in the catalytic stage.

The Arrhenius plot for temperature dependence (Figure 2) compares first stage thermal conversion activities in Runs 258, 260, 262 and 263 processing Black Thunder subbituminous coal operating in three different modes with supported, dispersed slurry and hybrid catalyst systems. The hybrid system with a combination of Molyvan L or 822 and Criterion 324 catalysts showed the highest thermal conversion activity, compared to the dispersed slurry and supported catalyst systems. The presence of Criterion supported catalyst in the second stage improved the resid + UC conversion in the first stage, due to improved hydrogenation by the supported catalyst in the second stage, producing better recycle process solvent and resulting in better thermal conversion in the first stage. It appears that the dispersed molybdenum catalyzes thermal hydrogenation of coal- and resid-derived free radicals³ through stabilization by hydrogen transfer from the process solvent, resulting in higher thermal conversion in the hybrid system. The dispersed catalyst system had a higher thermal conversion activity than the supported catalyst system. Apparent activation energies (30000-31000 Btu/lb-mole) for the hybrid and dispersed slurry systems were lower than that (53000-64000 Btu/lb-mole) for the supported catalyst system, although their conversion activity levels were higher than the supported system.

Figure 3 compares second stage conversion activities for Runs 262 and 263. The catalytic resid + UC conversion activity of the hybrid system with a combination of Molyvan L or 822 and Criterion 324 was much higher than the thermal conversion activity of the dispersed slurry catalyst system using Molyvan L or 822 alone. The calculated average rate constant values were 45-115% higher than those obtained without Criterion catalyst. The hybrid system catalytic activity was obtained with 3 lb/ton MF coal catalyst replacement. It seems that the dispersed molybdenum may not be greatly involved in hydrogenation and hydrocracking of the process solvent compared to the supported catalyst, since operations with the dispersed slurry catalyst gave significantly lower hydrogen and higher heteroatoms contents of distillate and process streams. It is possible that nickel or support material of the supported catalyst, which are missing components of the dispersed molybdenum, may play a significant role in hydrogenation and hydrocracking. Apparent activation energy for the hybrid catalyst system was 48000 Btu/lb-mole, higher than that with the supported catalyst (30000-40000 Btu/lb-mole). This high value might have been affected by molybdenum concentration variation in the range of 100-1000 ppm MF coal.

SOLIDS BUILDUP IN PROCESS LINES AND INTERSTAGE SEPARATOR

Problems associated with the formation of deposits in both the process lines and interstage separator between two reactors were discussed in the previous work processing subbituminous coals¹⁶, and two different solids deposition mechanisms suggested by Davis et al. were coking and mineral

deposition¹⁷. In recent Runs 262 and 263, the addition of Molyvan L or 822 as a dispersed slurry catalyst prevented reactor line plugging. However, solids did deposit in the interstage separator. A different interstage separator design could resolve the deposit problem.

DISTILLATE PRODUCT QUALITY

Table 3 summarizes distillate product qualities from Runs 258HI, 262E, 263EHJ, 257I and 261BD. During Run 259 with Pittsburgh coal and Shell 324, which was the first run tested with a better distillation separation system, the boiling end point of the distillate product was reduced to 715-760°F². In Run 261BD with Illinois coal and EXP-AO-60 bimodal catalyst, the end point was 772-780°F. Runs 257I and 258HI end point data were estimated by assuming steady recycle of heavy distillate as in Runs 259 and 261.

The major observation from Runs 262 and 263 in Table 3 was that operations in the hybrid system with a combination of Molyvan L or 822 and Criterion catalysts produced better quality distillate than just using dispersed slurry catalyst (periods 262E and 263J vs. 263EH). Hydrogen content increased to 11.0-11.4 wt %, while heteroatoms decreased to 0.6 wt % nitrogen and 1.7-2.1 wt % oxygen, respectively. The end point of the distillate product was similar for both catalyst systems (717-755°F). Note that the supported catalyst only system (258HI) had similar distillate product quality as the hybrid system. The presence of Criterion supported catalyst in the second stage seems to improve the product quality in both the hybrid and supported catalyst systems by increasing hydrogenation and heteroatoms removal.

CONCLUSIONS

- Processing Black Thunder subbituminous coal, the hybrid system with a combination of dispersed molybdenum slurry and supported catalysts improved the distillate production by 30-60% compared to using the dispersed slurry and supported catalysts separately.
- The addition of Molyvan L or 822 at a low 100 ppm MF coal as a dispersed molybdenum catalyst precursor significantly improved coal and resid conversions, allowing operation at lower thermal severity in the first stage and higher severity in the second stage compared to the supported catalyst system, resulting in higher C4+ distillate product yield and selectivity to resid + UC conversion.
- Operations in the hybrid system with a combination of Molyvan L or 822 and Criterion catalysts produced better quality distillate than just using dispersed slurry catalyst only. The boiling end point of the distillate product was similar for both catalyst systems (717-755°F).
- The supported catalyst only system had similar distillate product quality as the hybrid catalyst system. It seemed that the presence of Criterion supported catalyst in the second stage improved the product quality in both the hybrid and supported catalyst systems by increasing hydrogenation and heteroatoms removal.
- The dispersed molybdenum seemed to catalyze thermal hydrogenation of coal- or resid-derived free radicals through stabilization by hydrogen transfer from the process solvent, resulting in higher thermal conversion in the hybrid catalyst system, while seemed to have a less role in hydrogenation and hydrocracking of the process solvent compared to the supported catalyst.

- The addition of Molyvan L or 822 as a dispersed molybdenum catalyst precursor improved process operability by preventing reactor line plugging.
- Black Thunder subbituminous coal produced more distillate than Illinois No. 6 bituminous coal, when process operating conditions were optimized for better coal and resid conversions, even though the subbituminous coal had lower distillate yield and selectivity.

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TABLE 1. FEED COAL ANALYSIS
(BLACK THUNDER MINE - WYODAK ANDERSON SEAM)

FC: 49% mf, HV: 11800 Btu/lb mf, Reactives: 92 mmf vol%
Ultimate: 69.5% C, 5.1% H, 1.0% N, 0.6% S, 7.3% Ash, 16.5% O

TABLE 2. CATALYST PROPERTIES

Shell (or Criterion) 324 unimodal supported catalyst
1/16" size, 2.7% Ni, 13.2% Mo
SA: 165 m²/g, PV: 0.48 cc/g, CBD: 54 lb/ft³
Dispersed molybdenum slurry catalyst
Molyvan L: 8.1% Mo, 12.3% S, 6.4% P, no N
Molyvan 822: 4.9% 6.0% no yes

TABLE 3. TOTAL DISTILLATE PRODUCT QUALITY COMPARISON

Run Coal	258H	258I	262E	263E	263H	263J	257I	261B	261D
	-----Black Thunder-----						---Illinois---		
Wt % C	86.1	86.0	86.3	85.8	85.1	86.3	87.4	87.3	87.5
H	11.2	11.3	11.4	10.1	10.4	11.0	12.1	11.4	11.3
N	0.5	0.5	0.6	0.9	0.9	0.6	0.1	0.2	0.3
S	0.06	0.06	0.05	0.02	0.05	0.04	0.01	0.04	0.03
O (dir.)	2.2	2.2	1.7	3.9	3.6	2.1	0.4	1.1	0.9
°API	18	18	24	15	18	22	21	23	22
Wt % Naphtha	21	21	20	10	12	16	18	19	14
Mid.D1	15	15	10	14	17	14	11	11	16
Mid.D2	59	62	44	38	40	40	64	40	40
Gas Oil	5	2	26	38	31	30	7	30	30
End point °F (D1160)	667	665	748	755	719	717	665	772	780
	(estimated)						(est.)		

FIGURE 1 ORGANIC REJECTION VS COAL CONVERSION
Low-Rank Coal Correlation in CC-ITSL Process

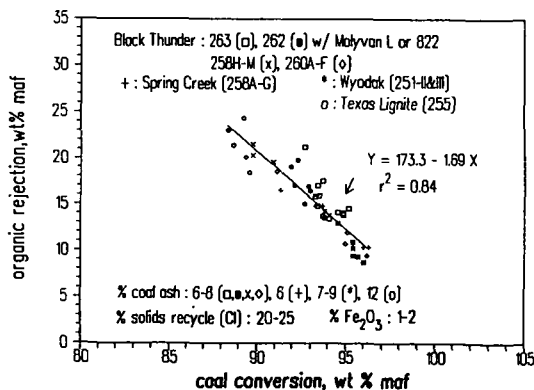


FIGURE 2

1ST STAGE THERMAL ACTIVITY COMPARISON (Black Thunder Subbituminous Coal)

Arrhenius Plot (CSTR 1st Order Resid+UC Conversion)

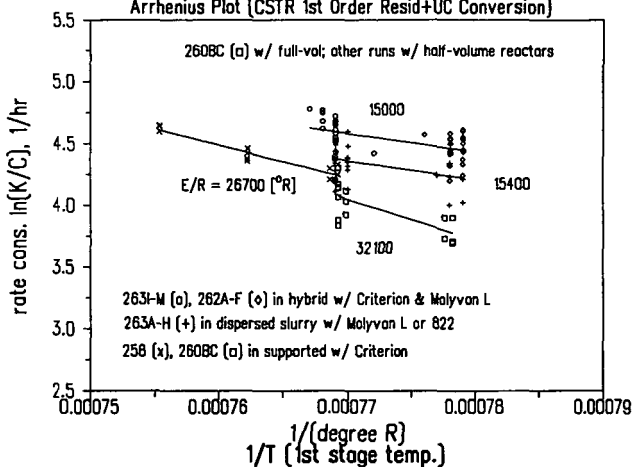


FIGURE 3

2ND STAGE CONVERSION ANALYSIS (RUNS 263,262)

Catalytic (Hybrid) vs. Thermal (Dispersed Slurry)

